

# TRANSMITTAL LETTER TO THE UNITED STATES DESIGNATED/ELECTED OFFICE (DO/EO/US) CONCERNING A FILING UNDER 35 U.S.C. 371

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10/031314

INTERNATIONAL APPLICATION NO.

PCT/US99/21708

INTERNATIONAL FILING DATE

September 20, 1999

PRIORITY DATE CLAIMED

TITLE OF INVENTION

FASTER CURING RUBBER ARTICLES

APPLICANT(S) FOR DO/EO/US

Carl Trevor Ross Pulford et al

Applicant herewith submits to the United States Designated/Elected Office (DO/EO/US) the following items and other information:

1. ☒ This is a **FIRST** submission of items concerning a filing under 35 U.S.C. 371.
2. ☐ This is a **SECOND** or **SUBSEQUENT** submission of items concerning a filing under 35 U.S.C. 371.
3. ☐ This is an express request to begin national examination procedures (35 U.S.C. 371(f)). The submission must include items (5), (6), (9) and (21) indicated below.
4. ☒ The US has been elected by the expiration of 19 months from the priority date (Article 31).
5. ☒ A copy of the International Application as filed (35 U.S.C. 371(c)(2))
  - a. ☐ is attached hereto (required only if not communicated by the International Bureau).
  - b. ☐ has been communicated by the International Bureau.
  - c. ☒ is not required, as the application was filed in the United States Receiving Office (RO/US).
6. ☐ An English language translation of the International Application as filed (35 U.S.C. 371(c)(2)).
  - a. ☐ is attached hereto.
  - b. ☐ has been previously submitted under 35 U.S.C. 154(d)(4).
7. ☒ Amendments to the claims of the International Application under PCT Article 19 (35 U.S.C. 371(c)(3))
  - a. ☐ are attached hereto (required only if not communicated by the International Bureau).
  - b. ☐ have been communicated by the International Bureau.
  - c. ☐ have not been made; however, the time limit for making such amendments has NOT expired.
  - d. ☒ have not been made and will not be made.
8. ☐ An English language translation of the amendments to the claims under PCT Article 19 (35 U.S.C. 371 (c)(3)).
9. ☒ An oath or declaration of the inventor(s) (35 U.S.C. 371(c)(4)).
10. ☐ An English language translation of the annexes of the International Preliminary Examination Report under PCT Article 36 (35 U.S.C. 371(c)(5)).

## Items 11 to 20 below concern document(s) or information included:

11. ☒ An Information Disclosure Statement under 37 CFR 1.97 and 1.98.
12. ☐ An assignment document for recording. A separate cover sheet in compliance with 37 CFR 3.28 and 3.31 is included.
13. ☐ A **FIRST** preliminary amendment.
14. ☐ A **SECOND** or **SUBSEQUENT** preliminary amendment.
15. ☐ A substitute specification.
16. ☐ A change of power of attorney and/or address letter.
17. ☐ A computer-readable form of the sequence listing in accordance with PCT Rule 13ter.2 and 35 U.S.C. 1.821 - 1.825.
18. ☐ A second copy of the published international application under 35 U.S.C. 154(d)(4).
19. ☐ A second copy of the English language translation of the international application under 35 U.S.C. 154(d)(4).
20. ☒ Other items or information:

International Search Report

10/031314

531 Rec'd PCT 15 JAN 2002

21. ☒ The following fees are submitted:**BASIC NATIONAL FEE (37 CFR 1.492 (a) (1) - (5)):**Neither international preliminary examination fee (37 CFR 1.482)  
nor international search fee (37 CFR 1.445(a)(2)) paid to USPTO  
and International Search Report not prepared by the EPO or JPO. ....

\$1040.00

International preliminary examination fee (37 CFR 1.482) not paid to  
USPTO but International Search Report prepared by the EPO or JPO .....

\$890.00

International preliminary examination fee (37 CFR 1.482) not paid to USPTO  
but international search fee (37 CFR 1.445(a)(2)) paid to USPTO .....

\$740.00

International preliminary examination fee (37 CFR 1.482) paid to USPTO  
but all claims did not satisfy provisions of PCT Article 33(1)-(4) .....

\$710.00

International preliminary examination fee (37 CFR 1.482) paid to USPTO  
and all claims satisfied provisions of PCT Article 33(1)-(4) .....

\$100.00

**ENTER APPROPRIATE BASIC FEE AMOUNT =****CALCULATIONS PTO USE ONLY**

\$ 890.00

Surcharge of \$130.00 for furnishing the oath or declaration later than ☐ 20 ☐ 30  
months from the earliest claimed priority date (37 CFR 1.492(e)).

\$

**CLAIMS****NUMBER FILED****NUMBER EXTRA****RATE**

\$

Total claims

9 - 20 =

0

x \$18.00

\$

Independent claims

1 - 3 =

0

x \$84.00

\$

**MULTIPLE DEPENDENT CLAIM(S) (if applicable)**

+ \$280.00

\$

**TOTAL OF ABOVE CALCULATIONS =**

\$

☒ Applicant claims small entity status. See 37 CFR 1.27. The fees indicated above  
are reduced by 1/2.

\$

+

**SUBTOTAL =**

\$

Processing fee of \$130.00 for furnishing the English translation later than ☐ 20 ☐ 30  
months from the earliest claimed priority date (37 CFR 1.492(f)).

\$

**TOTAL NATIONAL FEE =**

\$

Fee for recording the enclosed assignment (37 CFR 1.21(h)). The assignment must be  
accompanied by an appropriate cover sheet (37 CFR 3.28, 3.31). \$40.00 per property +

\$

**TOTAL FEES ENCLOSED =**

\$ 890.00

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- a. ☐ A check in the amount of \$ \_\_\_\_\_ to cover the above fees is enclosed.
- b. ☒ Please charge my Deposit Account No. 07-1725 in the amount of \$ 890.00 to cover the above fees.  
A duplicate copy of this sheet is enclosed.
- c. ☒ The Commissioner is hereby authorized to charge any additional fees which may be required, or credit any  
overpayment to Deposit Account No. 07-1725. A duplicate copy of this sheet is enclosed.
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**NOTE:** Where an appropriate time limit under 37 CFR 1.494 or 1.495 has not been met, a petition to revive (37 CFR  
1.137 (a) or (b)) must be filed and granted to restore the application to pending status.

SEND ALL CORRESPONDENCE TO:

SIGNATURE

Nancy T Krawczyk

NAME

38,744

REGISTRATION NUMBER

cc: J E Grillo

FASTER CURING RUBBER ARTICLES**Technical**

5           The present invention is directed toward curing methods for rubber articles. Specifically, the present invention discloses a method of producing faster curing rubber and more uniform cures in rubber articles.

**Background Art**

10           One of the many conflicting requirements of the rubber industry is for compounds that have a short cure time and a long scorch time. The conflict arises because scorch time cannot be changed independently of cure time; the times increase or decrease together. Conventionally, productive compounds, i.e. compounds that are capable of curing, are made in a Banbury mixer that generates heat in the compound during mixing. The compounds are then stored and subjected to further heat history during shaping of the compound by extrusion  
15 or calendering. The extruded or calendered article may be stored prior to application of the article in a larger green rubber article. The formed green article may also be further stored until curing. This entire process requires a certain minimum scorch time.

20           Reductions in cure times are proportional to increases in cure temperatures; however, reduced cure times can no longer be achieved by merely increasing the temperature of a curing press. Cure presses are conventionally run at the maximum temperature permitted to avoid overcure of the outside of the article while not exceeding any component cure limitations.

25           Today's compounds also have the shortest scorch time and shortest cure time allowed by the above discussed process. Compounds which have a relatively faster cure while maintaining scorch time have been sought and examples of rubber compositions with relatively reduced cure times are disclosed in U.S. Patents 4,755,320, 5,162,425, 5,238,991, 5,616,279, and 5,736,615.

30           US Patent 4,735,320 discloses a rubber composition with a specific cure package to achieve faster curing. For the disclosed exemplary compositions, the cure time for a ninety percent cure (T90) at 150° C ranges from 13.5 minutes down to 8.8 minutes. The scorch time at 150° C ranges from as low as 3.3 minutes to 5.4 minutes.

          US Patent 5,162,425 discloses a rubber composition with a standard cure package and an elastomeric blend to achieve faster curing of the rubber composition. For the disclosed exemplary compositions, T90 at 150° ranges from 12.5 to about 25 minutes; the scorch time ranges from a low of 5.3 to 7.3 minutes.

US Patent 5,238,991 discloses a composition with a cure package for achieving a fast curing elastomeric composition. For the disclosed exemplary compositions, T90 at 150° C ranges from 18.2 down to 8.8 minutes; the scorch times ranges from 2.6 to 6.4.

US Patents 5,616,279 and 5,736,615 disclose modifying the elastomer with a fast cure package. For the disclosed exemplary compositions, T90 at 150° C ranges from 14 down to 6 minutes; scorch times are 3.5 to 4.8 minutes.

To obtain a maximum scorch time for rubbers it is also known to not mix the cure package into the rubber compound until the rubber is to be used. The green rubber, absent a mixed cure package, may be stored indefinitely until it is needed for article manufacturing. When the green rubber is needed, the rubber is mixed in a Banbury with the appropriate cure package.

Another known alternative to extend the shelf life of the green rubber is to split the cure package. EP 496,202 discloses a two component system wherein the curatives are split between the two components. The two components must be masticated in a conventional mixer prior to use to achieve a thorough blend of the curatives and gain a productive compound.

US Patent 5,866,265 discloses a way to prevent scorch during extrusion of rubber microlayer compounds comprised of alternating layers of different rubber compositions. The cure package is split in any desired manner between the two different rubber compositions, the different compositions are kept separated in different barrels of the co-extruder until they are layered in the extruder die and the curatives migrate into the adjacent layers.

In order to use faster curing compounds in manufacturing rubber articles, the heat history imposed on productive compounds must be reduced. The present invention is directed toward overcoming the limitations of the prior art and producing even faster curing rubber compounds.

#### Summary of the Invention

The present invention is directed toward a method of producing faster curing rubber compounds than can be made by current factory mixing methods (Banbury or mill).

In the inventive method, an ultra fast curing elastomeric article comprising an elastomeric compound is produced. The elastomeric compound has a fast cure package comprising co-reacting agents. The cure package permits the elastomeric compound to achieve a ninety percent cure, at a cure temperature of 120° C, in less than 30 minutes. The ultra fast curing compound is produced by preparing two non-productive elastomer compounds, wherein each non-productive compound is prepared with a co-reacting agent of a co-reacting cure package not added to the other non-productive compound. The non-productive elastomer compounds are layered in alternating layers with a thickness relative to the diffusion rate of the co-reacting agents in each non-productive elastomeric layer to effect diffusion of the co-reacting cure agents through the adjacent layers to

form a layered compound. The layered compound is then cured to form the elastomeric article.

In one aspect of the disclosed method, the two-productives which are layered to permit diffusion of the co-reacting cure agents are formed of identical base compositions except for the co-reacting cure agents in each compound.

5 In another aspect of the disclosed method, the alternating layers of non-productive elastomer compounds are formed with a layer thickness equal or less than 2 mm. The layers may also be defined by differing thickness relative to each other.

In another aspect of the inventive method, the two non-productive compounds may be stored for any period of time prior to layering of the compounds to form the ultra-fast curing elastomer. In another aspect of the inventive method, the layered component may be stored for  
10 any period of time prior to curing the elastomer.

In one aspect of the inventive method, when preparing the two non-productives to be layered, the first non-productive compound is prepared with an absence of any accelerators found in the second non-productive compound and the second non-productive compound is prepared with  
15 an absence of any sulfur vulcanizing agent found in the first non-productive compound.

In another aspect of the invention, the first non-productive compound is prepared with 1 to 5 phr zinc oxide and 0 phr sulfur vulcanizing agent and the second non-productive compound is prepared with 0 phr zinc oxide and 0.2 to 8 phr sulfur vulcanizing agent.

In other aspects of the invention, the layered compound may be directly extruded into a  
20 desired final shape as it is beginning to cure, it may be extruded into final shape and then cured, or it may be applied to the surface of an article prior to curing the layered compound.

### **Brief Description of Drawings**

The invention will be described by way of example and with reference to the accompanying drawings in which:

25 FIG. 1 illustrates microlayering of a compound using a duplex extruder;

FIG. 2 illustrates the microlayered compound as it passes through a set of microlayering dies;

FIG. 3 illustrates a multilayering process;

FIG. 4 is a chart showing the MDR cure curves at 120° C for a series of layered  
30 rubber sheets; and

FIG. 5 is the MDR cure curves at 135° C for a series of layered rubber sheets.

### **Detailed Description of the Invention**

Through experimentation it has been determined that, unlike filler systems used in rubber compounds, curative packages do not need high mixing forces to be distributed within a

compound. Key curative chemicals conventionally used in rubber compounds (e.g. sulfur and accelerator) have an inherent solubility in rubber and can be uniformly distributed by diffusion. What is required is that the rubber compound be divided into regions that are small enough for the curatives to diffuse through the regions in the time available. The size of the regions is determined by the rate of diffusion in order to obtain a uniform distribution of the curative chemicals. It was discovered that the region size is small and can be preferably achieved by microlayering compounds without any further mastication. The compound may have a split cure package. The present invention is directed toward exploiting this discovery to greatly decrease the cure time of compounds without encountering scorch problems during processing of the compound.

Furthermore, it was also discovered that the cure package of conventional compounds can be replaced with known ultra-fast cure packages which will react in the layered diffusing method and avoid scorching of the rubber and decrease the cure time and temperature of the elastomeric compounds.

Microlayering may be achieved by the use of a duplex extruder 5 as illustrated in FIG. 1. The cure package for a reactive compound is split between two non-productives 10, 12 that have an "infinite" scorch time; that is, each non-productive 10, 12 is not capable of curing as compounded. Each non-productive 10, 12 is fed into a separate extruder 14, 16 of the duplex extruder 5. The non-productives 10, 12 are kept separate until the extruder die 18. A bi-layer of the two non-productives 10, 12 is generated inside the extruder die. The bi-layer is then fed through a series of microlayering die inserts 20, each of which doubles the number of layers in the extrudate. FIG. 2 illustrates the effect of feeding the two non-productives 10, 12 through the layering die inserts 20, and FIG. 3 illustrates the principle of the layering dies. A productive compound flows immediately through a shaping die 24 to form a tire component 22.

When the non-productives 10, 12 are layered inside the microlayering die inserts 20, the compounds are hot and therefore the rate of interdiffusion of the curatives may be fast. When interdiffusion begins to occur in the microlayering die inserts 20, an "in-situ" productive compound is created.

The curatives should be uniformly distributed throughout the in-situ productive compound so that the physical properties do not vary within the cured component. As the thickness of the adjacent layers is dependant upon the diffusion rate of the selected cure components in the cure package, the layer thickness in the microlayers should be sufficient to result in diffusion of the curatives through at least the adjacent layers. If the layers are too thick relative to the diffusion and cure rate, then curing may occur only at the layer boundaries. As the layer thickness decreases, the curatives diffuse through the layers more quickly and achieving

greater uniformity in the curative distribution. The thickness of the microlayers can be changed by varying the number of layering die inserts 20; layer thickness decreases with an increased number of die inserts 20. The number of layers is determined by the formula  $N=2 \times 2^n$ , where N equals the number of layers and n equals the number of die inserts. Preferably, the layer thickness should be about 2 mm or less to achieve the desired diffusion uniformity; however, given the variations in cure packages and diffusion rates of cure packages, the thickness may be greater.

The heat history seen by the in-situ productive compound is much less than that seen by conventionally processed compounds. The effective heat history seen by the in-situ compound occurs during its passage through the microlayering die inserts 20; any heat history seen by the non-productives 10, 12 during the mixing of the individual non-productives 10, 12 is irrelevant to the heat history of the in-situ productive compound. Therefore less scorch time can be tolerated and consequently, known faster curing compounds which can not be conventionally processed can be prepared in the inventive method disclosed.

For use in making in-situ productives 22, the use of the microlayer die inserts 20 and a profiling extruder results in the integration of static layering and profiling of a green rubber component. This integration allows for the creation of components of unprecedented fast cure properties, as further discussed below.

The microlayers may also be formed in a number of other ways than with the disclosed microlayer die inserts 20. Another method of co-extruding multilayer laminates is described in U.S. Pat. No. 3,557,165. Although extruders are a preferred means of preparing composites with large numbers of very thin layers (e.g. more than 10,000 layers/25.4 mm), other less elaborate means of preparing thin multilayers are also possible. A calender can be used to prepare thin sheets of polymeric material that can subsequently be plied up in alternating layers and possibly further thinned by application of pressure. By repeated plying and thinning, composites with several hundred layers per inch can be readily prepared.

Alternatively the small diffusion regions required for diffusion of the cure package may also be created by introducing the two non-productives 10, 12 in a duplex extruder with a static mixer type insert at the location where the two non-productives 10, 12 contact. The sole requirement, in accordance with the present invention is that the two non-productives 10, 12, after coming into contact, are reduced in size to the needed diffusion region size. Thus the defined layering of the invention can be accomplished by any alternating placement of non-productives 10, 12 so that the non-productives 10, 12 are in a contacting relationship to permit diffusion of the cure package. When placing the non-productives 10, 12 in a layering relationship, the non-productives 10, 12 may be configured as sheets, sticks, rods, strands,

planks, or similar configurations.

Each non-productive 10, 12 is comprised of a rubber compound. Representative rubbers that may be used in the rubber compound include acrylonitrile/diene copolymers, natural rubber, halogenated butyl rubber, butyl rubber, cis-1,4-polyisoprene, styrene-butadiene copolymers, cis-1,4-polybutadiene, styrene-isoprene-butadiene terpolymers ethylene-propylene terpolymers, also known as ethylene/propylene/diene monomer (EPDM), and in particular ethylene/propylene/dicyclopentadiene terpolymers. Mixtures of the above rubbers may be used. Each rubber layer may be comprised of the same rubber composition or alternating layers may be of different rubber composition.

The rubber compound may contain a platy filler. Representative examples of platy fillers include talc, clay, mica and mixture thereof. When used, the amount of platy filler ranges from about 25 to 150 parts per 100 parts by weight of rubber (hereinafter referred to as phr). Preferably, the level of platy filler in the rubber compound ranges from about 30 to about 75 phr.

The various rubber compositions may be compounded with conventional rubber compounding ingredients. Conventional ingredients commonly used include carbon black, silica, coupling agents, tackifier resins, processing aids, antioxidants, antiozonants, stearic acid, activators, waxes, oils, sulfur vulcanizing agents and peptizing agents. As known to those skilled in the art, depending on the desired degree of abrasion resistance, and other properties, certain additives mentioned above are commonly used in conventional amounts. Typical additions of carbon black comprise from about 10 to 150 parts by weight of rubber, preferably 50 to 100 phr. Typical amounts of silica range from 10 to 250 parts by weight, preferably 30 to 80 parts by weight and blends of silica and carbon black are also included. Typical amounts of tackifier resins comprise from about 2 to 10 phr. Typical amounts of processing aids comprise 1 to 5 phr. Typical amounts of antioxidants comprise 1 to 10 phr. Typical amounts of antiozonants comprise 1 to 10 phr. Typical amounts of stearic acid comprise 0.50 to about 3 phr. Typical amounts of accelerators comprise 1 to 5 phr. Typical amounts of waxes comprise 1 to 5 phr. Typical amounts of oils comprise 2 to 30 phr. Sulfur vulcanizing agents, such as elemental sulfur, amine disulfides, polymeric polysulfides, sulfur olefin adducts, and mixtures thereof, are used in an amount ranging from about 0.2 to 8 phr. Typical amounts of peptizers comprise from about 0.1 to 1 phr.

The key to the in-situ productive is the cure package. What is required is a suitable curative package that can be divided into two non-productives 10, 12 that will yield a faster than conventional cure when the two non-productives are alternately layered in the manner



previously described. The split of the cure package may also provide each resulting non-productive with an "infinite" shelf life or the layered component 22 with an "infinite" shelf life if curatives that are insoluble at low temperatures are employed. The need for the non-productives to have infinite shelf life is critical for some applications, such as retread cushion gum applications, because each non-productive or the layered component 22 must be capable of being stored for many months prior to use.

The current cure package can be split in a variety of ways depending on scorch safety requirements of the final product. Preferably sulfur will be located in one non-productive and accelerators in the other non-productive. Table 1 shows an example of an ultra-fast curing compound and how it is split into two non-productive compounds. Rubber compound A contains only curatives known not to induce cure in the absence of any cross-linking agents present, such as sulfur. Rubber compound B contains only sulfur, which will not crosslink to any great extent without the presence of the other curatives. Accelerator and sulfur levels were doubled in the split cure non-productives on the assumption that during diffusion of the curatives, the active curative intermediates would migrate across the multilayer interface and induce cure, thereby being "diluted" by half.

Certain combinations of sulfur and accelerators located in one non-productive and the remaining accelerators placed in the other non-productive would be permissible depending on the scorch safety requirements needed for final component fabrication. One skilled in the art would know the scorch safety requirements and choose the appropriate combination. For example in Table I, N,N'-diphenylguanidine/2-mercaptobenzothiazole/zinc dibenzyl dithiocarbamate is in compound A and sulfur is in compound B. This is the most advantageous for scorch safety. Other possible splits include the combination of the addition of sulfur/zinc dibenzyl dithiocarbamate in compound B and N,N'-diphenylguanidine/2-mercaptobenzothiazole in compound A, the combination of the addition of N,N'-diphenylguanidine/sulfur in B and zinc dibenzyl dithiocarbamate/2-mercaptobenzothiazole in A, the combination of the addition of N,N'-diphenylguanidine /zinc dibenzyl dithiocarbamate/sulfur in B and 2-mercaptobenzothiazole in A, and the combination of the addition of 2-mercaptobenzothiazole/sulfur in B and N,N'-diphenylguanidine /zinc dibenzyl dithiocarbamate in A. It is also to be understood that the fast cure packages disclosed in the previously discussed U.S. Patents 4,755,320, 5,616,279, and 5,736,615, all commonly assigned to The Goodyear Tire & Rubber Company, the assignee of the instant invention, may be used in the present invention. Other combinations include the selection of cure agents that are insoluble but become soluble within a trigger range temperature and which will then

diffuse into the adjacent layers.

Table 1 shows the ODR cure rheometer data for an exemplary compound. The ultra-fast curing compound has a scorch time of 2.8 min at 120° C. The ultra-fast curing compound was mixed by passing the compound, by hand, through a cold mill as the compound would have scorched if mixed in a Banbury. Neither of the split cure rubber compounds A and B exhibited any cure.

Table 1

	Compound		
	Ultra-Fast Compound	Rubber Compound A	Rubber Compound B
Blend of Rubber & fillers, phr <sup>1</sup>	171.3	171.3	171.3
N,N'-diphenylguanidine, phr	0.5	1	
Insoluble sulfur (amorphous sulfur), phr	2.8		5.6
2-mercaptobenzo-thiazole, phr	0.85	1.7	
Zinc dibenzyl dithiocarbamate, phr	1	2	
	ODR Rheometer Results 120° C for 60 minutes		
T90 <sup>2</sup>	15	no cure	no cure
T80 <sup>3</sup>	8		
T25 <sup>4</sup>	4		
T(1) <sup>5</sup>	2.8		

<sup>1</sup> 100 phr Natural Rubber and 40 phr carbon black

<sup>2</sup> Time to achieve a 90% cure of the compound

<sup>3</sup> Time to achieve an 80% cure of the compound

<sup>4</sup> Time to achieve a 25% cure of the compound

<sup>5</sup> Scorch time

For non-productives requiring an infinite shelf life, the sulfur-donor class of

accelerators was excluded because, although they provide for ultra fast curing, they are capable of curing rubber on their own and therefore cannot make an indefinite shelf life non-productive. In other applications of the present invention wherein a long shelf life for the non-productive is not required, such as for new tires, it is understood that other classes of accelerators could be used. Suitable types of accelerator classes would include amines, aldehyde/amine (condensation reaction products), disulfides, guanidines, thioureas, thiozoles, thiurams, sulfenamides, dithiocarbamates, and xanthates.

For comparison with the hand mixed ultra-fast compound, the split-cure rubber compounds A and B were microlayered together to create several in-situ productives as follows. Productive sheets, about 7 inches (about 178 mm) wide and 1/8 inches (3.175 mm) thick, were made containing 8 and 32 alternating horizontal layers of the split-cure non-productives. The thickness of the layers of split-cure non-productives in the productive sheets was therefore 0.015 inches (0.4mm) and 0.004 inches (0.1mm) respectively. For the 8-layer sheets, the die set temperature was 210° F. For the 32-layer sheets, die temperatures of 210° F and 270° F were used. The duplex extruder screws were both run at 10 RPM in order to obtain a productive with a 50/50 composition of the two split-cure non-productives, Compound A and B. The sheets obtained at the 210° F die set temperature buckled due to unequal shrinkage, but at the 270° F die temperature, the nerve was reduced and smooth sheets were obtained. Signs of scorch were not seen in any of the sheets.

Samples of the sheet were cut and immediately quenched in ice water to stop any cure that might have begun and the samples were tested using cure rheometers. Multiple samples were taken during each extrusion condition, in order to assess the uniformity of cure during a run of the extruder.

In preparing the productive compound using the previously discussed microlayering die inserts 20, the minimum number of layering inserts required to give a uniform dispersion of curatives should be employed since the extruder head pressure increases with the number of inserts.

As a benchmark, samples of the 8-layer and 32-layer sheets were passed through a cold mill ten times by hand without banding, in order ensure complete dispersion of the curatives. These samples represent the final, "equilibrium" state of curative dispersion. The cure rheometer curves of the microlayered stocks and those that had been milled were measured at two temperatures, 120 C° and at 135 C°, using both ODR and MDR cure rheometers. Graphs of the MDR cure curves are illustrated in FIGS 4 and 5; the cure information is also set forth in Table 2.

Condition	ODR Cure Rheometer Data			MDR Cure Rheometer Data		
	Scorch time at 120° C (min) <sup>1</sup>	T90 at 120° C (min) <sup>2</sup>	T90 at 135° C (min) <sup>3</sup>	Scorch Time at 120° C (min) <sup>1</sup>	T90 at 120° C (min) <sup>2</sup>	T90 at 135° C (min) <sup>3</sup>
8-layer Sheet	3.3 +/- 0.3	15.3 +/- 2.5	5.65 +/- 0.6	3.6 +/- 0.22	18.09 +/- 1.2	7.22 +/- 1.0
8-layer Sheet - 10 mill passes	2.5 +/- 0	10.5 +/- 0	4.8 +/- 0	3.5	12.17	3.97
32 layer sheet	2.9 +/- 0.14	10.5 +/- 0	4.8 +/- 0			
32 layer sheet - die temp 210° F				2.285 +/- 0.02	15.99 +/- 0.18	4.98 +/- 0
32 layer sheet - die temp 210° F - 10 mill passes				2.2	15.8	4.77
32-layer sheet - die temp 270° F	2.85 +/- 0.5	10.25 +/- 0.35	3.5 +/- 0.25	2.73 +/- 0	15.95 +/- 0.45	4.71 +/- 0.22
32-layer sheet - die temp 270° F - 10 mill passes	3.3 +/- 0	10.5 +/- 0	---	2.62	15.45	4.08

<sup>1</sup> Time to achieve 1% cure of the compound; i.e. T(1)<sup>2</sup> Time to achieve 90% cure of the compound at a cure temperature of 120° C<sup>3</sup> Time to achieve 90% cure of the compound at a cure temperature of 135° C

Table 2

Cure properties were determined using a Monsanto oscillating disc rheometer which was operated at a temperature of 120° C and 135° C and at a frequency of 11 hertz. A description of oscillating disc rheometers can be found in the Vanderbilt Rubber Handbook edited by Robert O. Ohm (Norwalk, Conn., R. T. Vanderbilt Company, Inc., 1990), pages 554-557. The use of this cure meter and standardized values read from the curve are specified in ASTM D-2084. A typical cure curve obtained on an oscillating disc rheometer is shown on page 555 of the 1990 edition of the Vanderbilt Rubber Handbook.

The cure time of the productive sheets was exceptionally short. The 32-layer sheet has a ninety percent cure (T90), at 135° C, of 4 minutes. At 120 C°, the ODR cure time was typically 10.5 min for the 32-layer sheet, longer than the cure at 135°C as would be expected. The scorch time of the 32-layer sheet was about 3 minutes. The conventional process of Banbury mixing followed by calendering could not be used to make this sheet, as the sheet would scorch. This cure time is exceptionally short compared to conventional elastomeric compounds. Conventional rubber compounds have an average T90 of 30 minutes at 120° C, or an average T90 of about 10-20 minutes at 150° C. The cure time of the 32-layer sheet is also less than the cure time of the fast curing elastomers of the prior art, while maintaining a comparable or slightly less scorch time at the lower curing temperature.

The cure time of the compound when prepared as a 32-layered sheet is less than when the compound is prepared by hand milling, see Tables 1 and 2; the cure time is reduced from 15 minutes to about 10 minutes, a 1/3 reduction in cure time. However, the scorch time of the compound stayed substantially the same; when prepared by hand mill, T(1) was 2.8 minutes, when prepared by layering, average T(1) was 2.87 minutes.

What this indicates is that by processing the compound in a multi-layering process using a split cure package, the time to cure rubber compounds can be significantly reduced, and a desirable scorch time may be maintained, as demonstrated by the cure times in Table 2.

Thus the goal of achieving a faster curing elastomeric compound is achieved by microlayering the two non-productives in the manner described. The desirable goal of achieving a faster cure at a lower curing temperature is also achieved. As cure times decrease with increased cure temperature, where the above microlayered compound cured at the conventional curing temperature of 150° C, cure times would be almost instantaneous, faster than the known cure times at 150° C for the above disclosed fast cure elastomers.

The 120 C° ODR cure rheometer curves of 32-layer samples taken throughout the run superposed on each other suggests that the composition of the cure package created in the microlayer extruder was very consistent. Also, the ODR and MDR cure results indicate that

the curatives diffuse between the microlayers to create an in-situ productive. The diffusion of the curatives is complete in the 32 layer sheets, as indicated by the identical cure curves of the 32-layer sheet and the milled 32-layer sample (where the distribution of curatives is uniform). In contrast, the diffusion process is not complete in the 8-layer sheet as indicated by the longer  
5 cure time that is longer than for the 32-layer sheet and is shortened by milling. The cure time of the milled 8-layer sheet is identical to the unmilled 32-layer sheet; this is again consistent with the 32-layer sheet having the equilibrium distribution of curatives. The results indicate that the microlayer thickness of 0.004 inches (0.1mm) is small enough for complete interdiffusion of these particular curatives to occur in this rubber blend, but that 0.015 inches  
10 (0.4mm) is not thin enough for the exemplary cure package containing insoluble sulfur. As previously discussed, the thickness of the layers is dependent upon the diffusion rate of the curatives, and will vary with different cure packages.

The degree of cure of the microlayered, in-situ productive with layer thickness about 0.1mm is very close to that of the ultra-fast compound of Table 1. This indicates that the  
15 microlayer process for creating in-situ productive delivers the same cured compound as the hand pass/cold mill process.

Also, these results point to the ability to produce faster curing "infinite" shelf life components. As disclosed, one constituent of the split cure package may be of the type that is insoluble at standard mixing temperatures but changes into a soluble constituent when heated  
20 to a temperature within a trigger temperature range; the trigger temperature range is dependent upon different factors such as the curatives used, and any cure intermediates created. In preparing an "infinite" shelf life component 22, one of the non-productives 10 or 12 is prepared with an insoluble curative constituent and the other non-productive 12 of 10 is prepared with the co-reacting curative. The non-productives 10, 12 are microlayered in the  
25 manner disclosed above, and may be extruded into a shaped component 22. Since neither the non-productives 10, 12 nor the microlayered component 22 have been subjected to a temperature sufficient to convert the insoluble curative capable of beginning to diffuse through the layers, the microlayered component 22 does not begin curing and has an "infinite" shelf life. When it is desired to use the microlayered component 22, the component 22 is then  
30 subjected to a temperature within the trigger temperature range sufficient to convert the curative to a diffusable state and begin cure of the component. Due to the faster cure chemistry of the then soluble cure agents, the component 22 will cure at a faster rate than is conventionally seen in the compound.

The in-situ productive technology allows compound sheets to be made of ultra-high speed cure properties at lower than conventional temperatures. Such high cure rates are not achievable by existing conventional processes. The results found suggest multiple applications of the lower temperature and ultra fast curing rubber production method in the compound and rubber industry. The inventive method may be useful in manufacturing a variety of non-reinforced rubber products that can be formed by extrusion.

The above results also indicate that tailoring of the cure kinetics of the in-situ productive may be achieved. This is achieved by adjusting the screw speed of the two extruders 10, 12 relative to each other during the wind of the productive 22. The variance of the screw speeds may be synchronized with the thickness of the productive 22, or the thickness of the article that is being built up with the extruded productive 22. Varying the screw speeds results in each non-productive having a different layer thickness. When using the in-situ productive as a thick article, it may also be desired to match the cure kinetics with the temperature/time history to be seen at each and every location in the curing of the thick part; thereby providing a uniform degree of cure throughout the thick article. Tailoring of the cure kinetics is useful in manufacturing such articles as heavy tires such as off the road, agricultural, and industrial tires as well as thick engineered products such as heavy conveyor belting and rubber bridge bearings.

One application for the in-situ productive compound include the use of the faster curing in-situ compound as components of large rubber articles, such as belting including conveyor belting, airsprings, rubber tracks, passenger tires, truck tires, agricultural tires, large earth moving tires or extended mobility tires which require thick sidewall inserts. The in-situ compound is particularly useful for articles wherein the cure time of the article is determined by the cure rate at the "point of least cure." For new tires, the use of in-situ productives for internal components (e.g. EMT insert, apex, shoulder wedge) removes the bottleneck of curing the internal thick component to reduce cure times and increase productivity. In heavy tires, where the tire components are strip wound, such as in off the road, earth moving, and farm tires, in-situ productive technology might allow the internal regions to be made with much faster cure properties than external regions. As discussed above, by changing the relative outputs of the two extruders, the cure package could be adjusted during the wind, so as to tailor the cure kinetics of the productive to its position in the tire, as discussed above.

Another embodiment to obtain a more uniform and rapid cure in articles which are made from extruding thick profiles rather than being built-up by winding strips would be to use triplex or quadraplex extruders wherein three or four extruders feed the same head and die system. One extruder would deliver a conventional, slow-curing compound, which would pass through a

conventional insert and die system. This compound would occupy the region of the profile that would be in contact with the hot mold during curing. The other extruders would deliver split-cure compounds, which would be combined in a microlayer or static mixer die insert to form fast-curing productives. These would occupy the region of the profile that will be away from the hot mold. The resulting profile (e.g. tire tread or sidewall) would have a tailored cure rate, which varies from slow, where it contacts the hot mold, to very fast in regions furthest from the hot mold.

Other applications for the in-situ productive compound include the use of in-situ compounding for outer layers of articles. When using the in-situ productive, the curing temperature of the complete article can be reduced; this is especially useful if any of the other components of the article are temperature sensitive and cannot be cured at high temperatures or cannot be exposed to curing temperatures for an extended period of time. The in-situ productive may also be used as a patch to repair articles. Using the productive as a patch allows for either an "infinite" shelf life and/or for more rapid repairs to a variety of articles, such as tires, beltings, rubber tracks, and a variety of other articles that have an outer elastomeric layer.

Those skilled in the art would readily appreciate that the applicability of in-situ productive technology in other related fields, wherever faster cure times are desired and are currently limited by the conventional technology.



## CLAIMS

1. An improved method of producing an ultra fast curing elastomeric article of the type comprising an elastomeric compound, the elastomeric compound comprising a fast cure package of co-reacting agents wherein the compound achieves ninety percent cure, at a cure temperature of 120° C, in less than 30 minutes, wherein the improvement comprises
  - a) preparing two non-productive elastomer compounds (10, 12), wherein each non-productive compound (10 or 12) is prepared with a co-reacting agent of a co-reacting cure package not added to the other non-productive compound (12 or 10),
  - b) layering the non-productive elastomer compounds (10, 12) in alternating layers with a thickness relative to the diffusion rate of the co-reacting agents in each non-productive elastomeric layer to effect diffusion of the co-reacting cure agents through the adjacent layers to form a layered compound and
  - c) curing the layered compound (22) to form the elastomeric article.
2. A method of producing an ultra fast curing elastomeric article in accordance with claim 1, the method being characterized by preparing the two non-productive compounds (10, 12) with identical compositions except for the co-reacting cure agents in each compound (10, 12).
3. A method of producing an ultra fast curing elastomeric article in accordance with claim 1, the method being characterized by forming each adjacent layer with a thickness equal or less than 2 mm.
4. A method of producing an ultra fast curing elastomeric article in accordance with claim 1, the method being characterized by layering the two non-productive elastomer compounds (10, 12) with differing thickness'.
5. A method of producing an ultra fast curing elastomeric article in accordance with claim 1, the method being characterized by the further step of storing the two non-productive compounds (10, 12) for a period of time prior to layering.
6. A method of producing an ultra fast curing elastomeric article in accordance with claim 1, the method being characterized by forming the first non-productive compound (10 or 12) with an absence of any accelerators found in the second non-productive compound (12 or

10) and forming the second non-productive compound (12 or 10) with an absence of any sulfur vulcanizing agent found in the first non-productive compound (10 or 12).

5 7. A method of producing an ultra fast curing elastomeric article in accordance with claim 1, the method being characterized by forming the first non-productive compound (10 or 12) with 1 to 5 phr zinc oxide and 0 phr sulfur vulcanizing agent and forming the second non-productive compound (12 or 10) with 0 phr zinc oxide and 0.2 to 8 phr sulfur vulcanizing agent.

10 8. A method of producing an ultra fast curing elastomeric article in accordance with claim 1, the method being characterized by forming one non-productive elastomer compound (10 or 12) with a sulfur vulcanizing agent that is non-soluble when the two non-productive elastomer compounds (10 or 12) are layered and which converts to a diffusable state prior to curing of the layered compound (22).

15 9. A method of producing an ultra fast curing elastomeric article in accordance with claim 1, the method being characterized by applying the layered compound (22) on the surface of an article prior to curing the layered compound (22).

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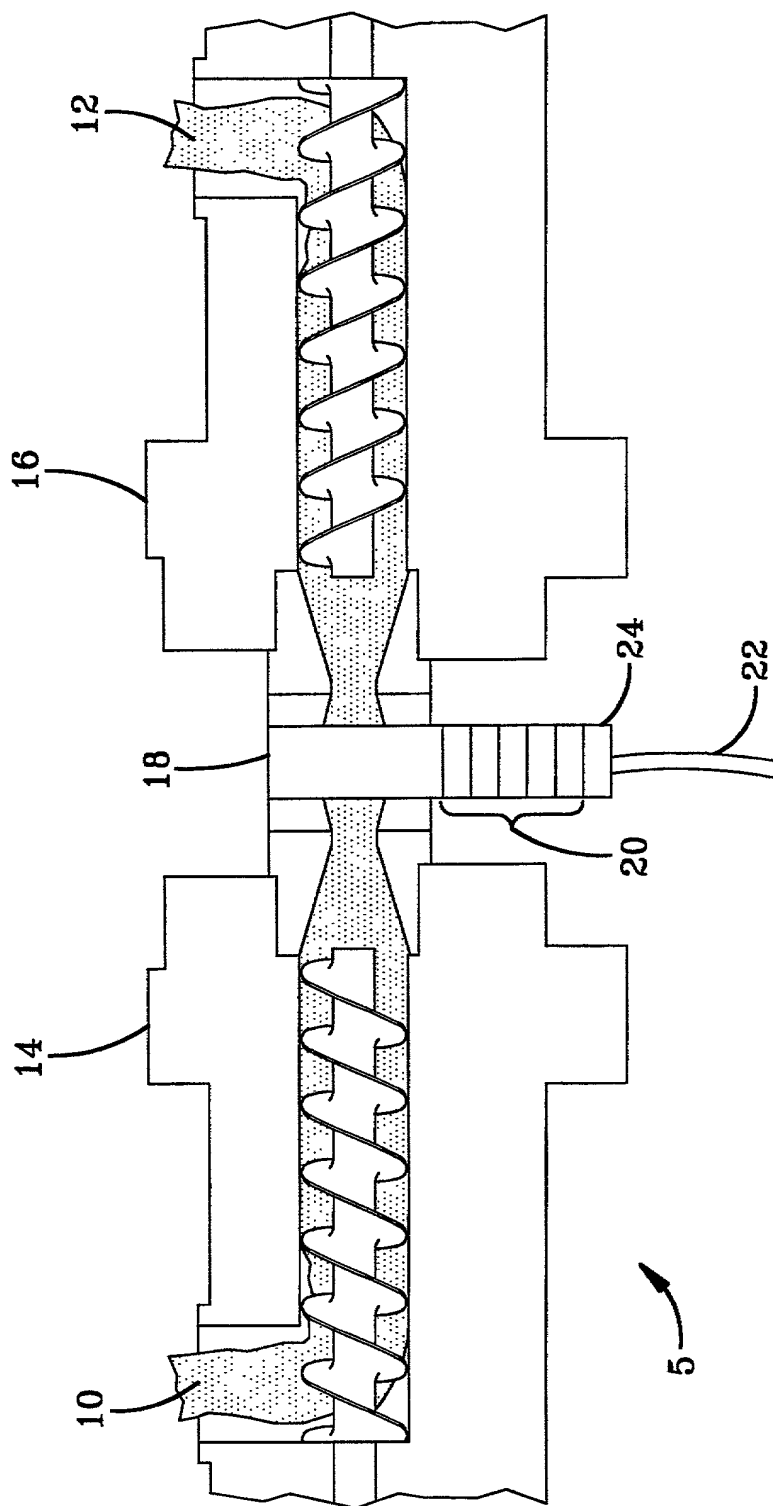


FIG-1

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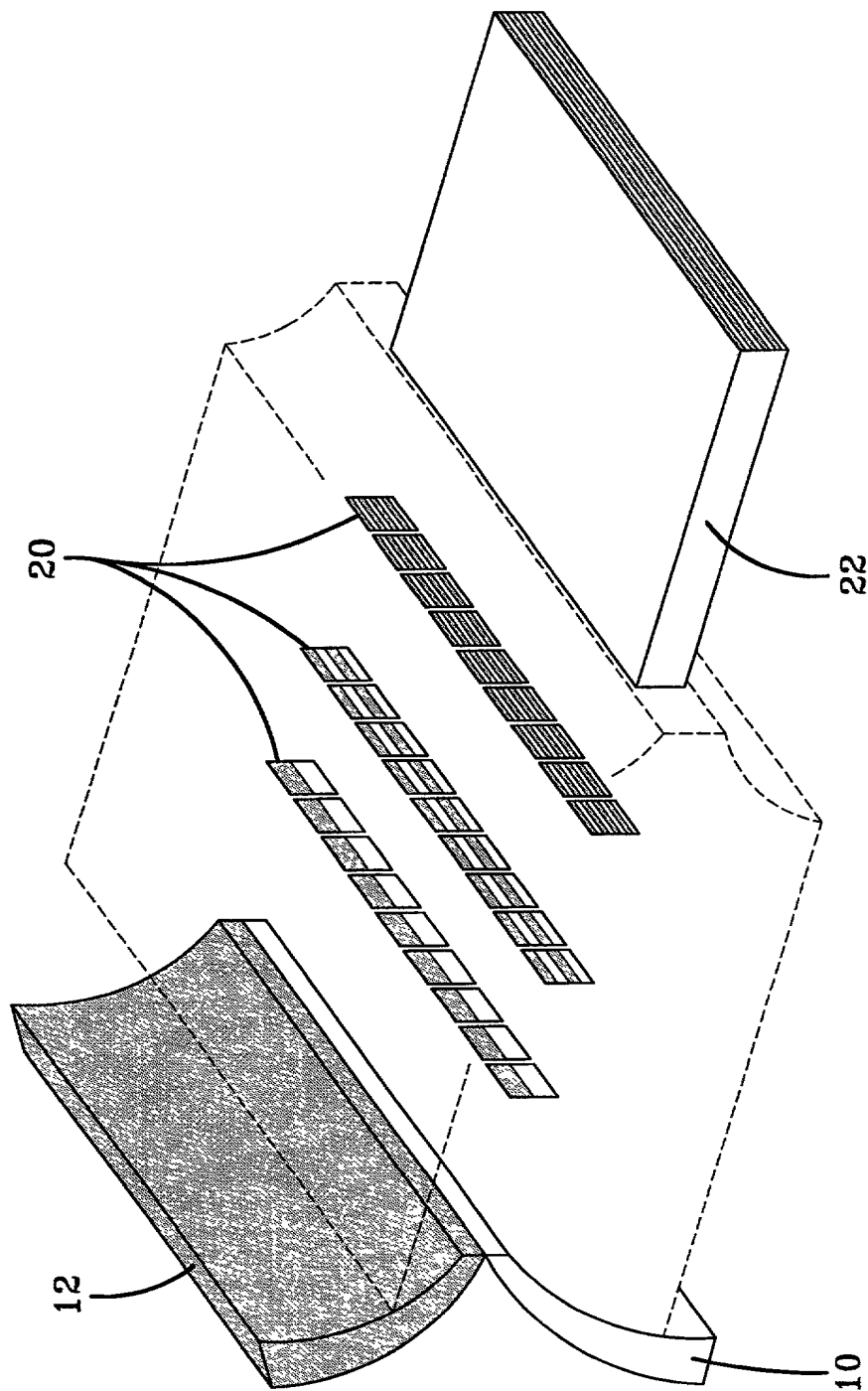


FIG-2

# MULTILAYER PROCESS AND DIE OPERATION

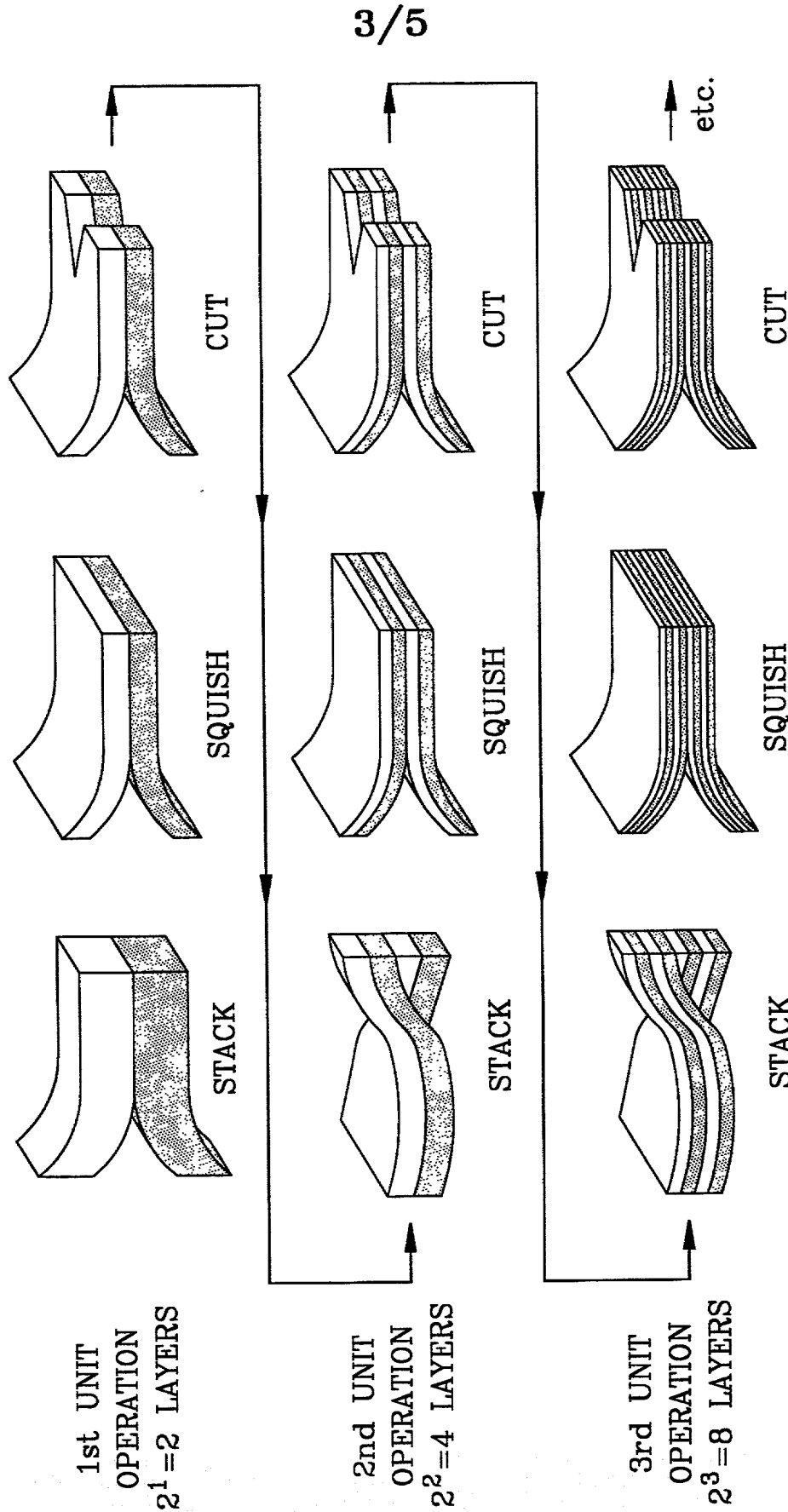
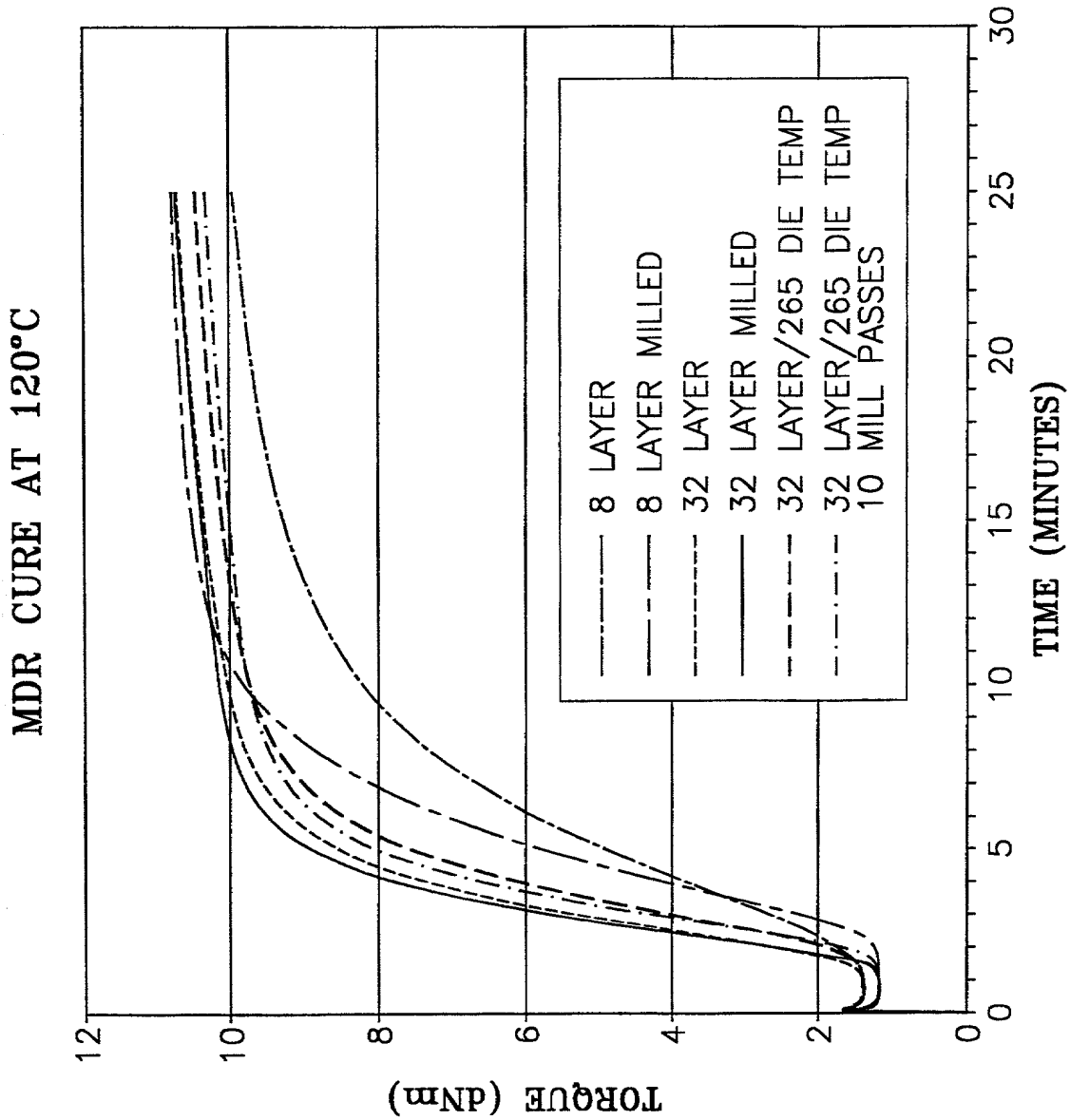


FIG-3

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MDR CURE AT 135°C

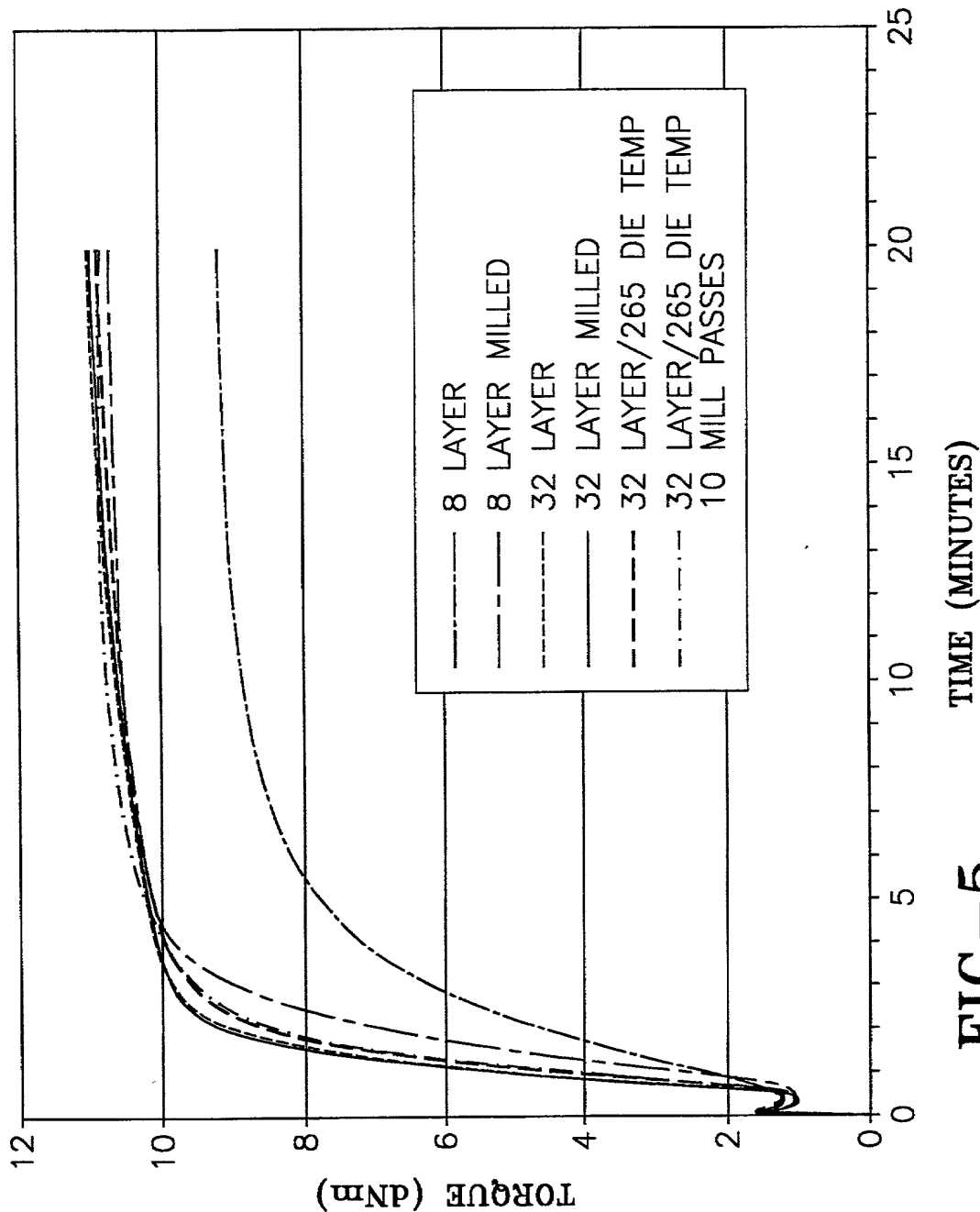


FIG-5

**DECLARATION AND POWER OF ATTORNEY**

As a below named inventor, I hereby declare that:

My residence, post office address and citizenship are as stated below next to my name.

I believe I am the original, first and sole inventor (if only one name is listed below) or an original, first and joint inventor (if plural names are listed below) of the subject matter which is claimed and for which a patent is sought on the invention entitled **FASTER CURING RUBBER ARTICLES** the specification of which (check one)

       a copy is attached hereto.

       X was filed on September 20, 1999 as Application Serial No. PCT/US99/21708  
and was amended on        (if applicable).

I hereby state that I have reviewed and understand the contents of the above identified specification, including the claims, as amended by any amendment referred to above.

I acknowledge the duty to disclose information which is material to patentability as defined in 37 C.F.R. §1.56.

I hereby claim the benefit under 35 U.S.C. §119(e) of any United States provisional application(s) listed below:

(Application Serial No.)

(Filing Date)

(Application Serial No.)

(Filing Date)

I hereby claim the benefit under 35 U.S.C. §120 of any United States application(s) or §365 of any PCT International application designating the United States, listed below and, insofar as the subject matter of each of the claims of this application is not disclosed in the prior United States or PCT International application in the manner provided by the first paragraph of 35 U.S.C. §112, I acknowledge the duty to disclose material information as defined in 37 C.F.R. §1.56 which become between the filing date of the prior application and the national or PCT international filing date of this application:

(Application Serial No.)

(Filing Date)

(Status)(patented, pending, abandoned)

(Application Serial No.)

(Filing Date)

(Status)(patented, pending, abandoned)

**POWER OF ATTORNEY**

As named inventor(s), I or we hereby appoint the following attorney(s) and/or agent(s) to prosecute this application and transact all business in the Patent and Trademark Office connected therewith.

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I hereby declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under section 1001 of Title 18 of the United States Code, and that such willful false statement may jeopardize the validity of the application or any patent issuing thereon.

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